(c) $\ln \frac{1}{0.60} = 0.00228\ \text{min}^{-1} \times t$; $t = 224$ min

(d) $\ln \frac{1.58 \times 10^{-2}\ \text{min}^{-1}}{2.28 \times 10^{-2}\ \text{min}^{-1}} = \frac{E_a}{0.00831}\left(\frac{1}{298} - \frac{1}{313}\right)$; $E_a = 1.00 \times 10^2$ kJ

(e) At 25°C: rate = $0.00228\ \text{min}^{-1} \times 0.100\ M = 2.28 \times 10^{-4}\ M/\text{min}$

At 40°C: rate = $0.0158\ \text{min}^{-1} \times 0.100\ M = 1.58 \times 10^{-3}\ M/\text{min}$

$\frac{1.58 \times 10^{-3}}{2.28 \times 10^{-4}} = 6.93$; hence, approximately 7 times faster

(f) At 25°C: $\ln \frac{1}{0.35} = 0.00228\ \text{min}^{-1} \times t$; $t = 460$ min

At 40°C: $\ln \frac{1}{0.35} = 0.0158\ \text{min}^{-1} \times t$; $t = 66.4$ min

460 − 66.4 = 394 min longer

PROBLEMS

1. (a) rate = $\frac{-\Delta [C_2H_6]}{2\Delta t}$ (b) rate = $\frac{\Delta [CO_2]}{4\Delta t}$

3. (a) rate = $\frac{-\Delta [X]}{\Delta t} = \frac{\Delta [Y]}{\Delta t}$

Time (min)	0	20	40	60	80
moles Y	0	0.017	0.035	0.049	0.054

(b) rate = $\frac{-\Delta [X]}{\Delta t} = \frac{-(0.103 - 0.120)\ \text{mol}}{(20 - 0)\ \text{min}} = 8.5 \times 10^{-4}$ mol/min

(c) rate = $\frac{\Delta [Y]}{\Delta t} = \frac{(0.049 - 0.017)\ \text{mol}}{(60 - 20)\ \text{min}} = 8.0 \times 10^{-4}$ mol/min

5. rate = $\frac{\Delta [CO_2]}{\Delta t} = \frac{4\Delta [C_2H_6]}{\Delta t} = 4(0.2\ M/\text{s}) = 0.8\ M/\text{s}$

rate = $\frac{\Delta [H_2O]}{\Delta t} = \frac{6\Delta [C_2H_6]}{\Delta t} = 1.2\ M/\text{s}$

7. (a) $2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g)$

(b) rate = $\frac{-\Delta [NOCl]}{2\Delta t}$

(c) rate = $\frac{(0.238 - 0.580)\ M}{2(8)\ \text{min}} = -\ 0.0214\ M/\text{min}$

9. (b) $\approx$ 0.003 mol/L·s

(c) $\text{rate} = \dfrac{-(0.14 - 0.24)\,M}{(40 - 10)\text{ s}} = 0.0033\ M/\text{s}$

(d) The instantaneous rate is slightly less.

11. (a) 3rd order in A

(b) 1st order in A; 1st order in B; 2nd order overall

(c) 1st order in A; 2nd order in B; 3rd order overall

(b) 1st order in B

13. (a) $\dfrac{\text{mol/L} \cdot \text{min}}{(\text{mol/L})^3} = \dfrac{\text{L}^2}{\text{mol}^2 \cdot \text{min}}$

(b) $\dfrac{\text{mol/L} \cdot \text{min}}{(\text{mol/L})^2} = \dfrac{\text{L}}{\text{mol} \cdot \text{min}}$

(c) $\dfrac{\text{mol/L} \cdot \text{min}}{(\text{mol/L})^3} = \dfrac{\text{L}^2}{\text{mol}^2 \cdot \text{min}}$

(d) $\dfrac{\text{mol/L} \cdot \text{min}}{\text{mol/L}} = \dfrac{1}{\text{min}}$

15. (a) linear graph; first-order reaction

(b) rate = k [X]

(c) 0.0050 M/min = k(0.1 M); k = 0.050 min^{-1}

17. (a) rate = k [R][S]^2 = (1.49 L^2/mol^2 · min) $\times$ (0.200 mol/L) $\times$ (0.200 mol/L)^2 = 0.0119 mol/L·min

(b) $[\text{R}] = \dfrac{0.833\text{ mol/L} \cdot \text{min}}{(0.42\text{ L}^2/\text{mol}^2 \cdot \text{min})(0.633\text{ mol/L})^2} = 4.9\text{ mol/L}$

(c) $[\text{S}]^2 = \dfrac{0.162\text{ mol/L} \cdot \text{min}}{(0.298\text{ L}^2/\text{mol}^2 \cdot \text{min})(0.100\text{ mol/L})}$; [S] = 2.33 mol/L

(d) $k = \dfrac{0.00624\text{ mol/L} \cdot \text{min}}{(0.0500\text{ mol/L})(0.0911\text{ mol/L})^2} = 15.0\text{ L}^2/\text{mol}^2 \cdot \text{min}$

19. (a) rate = $k\,[NO_2]^2$

(b) $k = \dfrac{1.17\text{ mol/L} \cdot \text{min}}{(0.250\text{ mol/L})^2} = 18.7\text{ L/mol·min}$

(c) rate = 18.7 L/mol·min $\times$ (0.800 mol/L)^2 = 12.0 mol/L·min

21. rate = $k[NO]^2[Br_2]$

(a) $k = \dfrac{1.6 \times 10^{-8}\text{ mol/L} \cdot \text{min}}{(0.020\text{ mol/L})^2(0.030\text{mol/L})} = 0.0013\text{ L}^2/\text{mol}^2\text{·min}$

(b) $[Br_2] = \dfrac{3.5 \times 10^{-7}\text{ mol/L} \cdot \text{min}}{(0.0013\text{ L}^2/\text{mol}^2 \cdot \text{min})(0.043\text{ mol/L})^2} = 0.15\text{ mol/L}$

(c) $[Br_2] = \dfrac{[NO]}{4}$; $[NO]^2 = \dfrac{\text{rate}}{k} \times \dfrac{1}{[Br_2]} = \dfrac{2.0 \times 10^{-6}\text{ mol/L} \cdot \text{min}}{0.0013\text{L}^2/\text{mol}^2 \cdot \text{min}} \times \dfrac{4}{[NO]}$; [NO] = 0.18 mol/L

23. (a) $0.0167/0.0107 = (0.100/0.0800)^m$; $1.56 = 1.25^m$; $m = 2$

(b) rate = $k[A]^2$

(c) 0.0167 mol/L·min = k(0.100 mol/L)^2; k = 1.67 L/mol·min

25. (a) rate = $k \times [S_2O_8^{2-}]^m \times [I^-]^n$

$2.22/1.85 = (0.0300/0.0250)^m$; $1.20 = 1.20^m$; $m = 1$

$3.06/2.22 = (0.0275/0.0200)^n$; $1.38 = 1.38^m$; $n = 1$

1st order in $S_2O_8^{2-}$; 1st order in I^-; 2nd order overall

(b) rate = $k \times [S_2O_8^{2-}] \times [I^-]$

(c) $k = \dfrac{1.15 \times 10^{-4}\text{ mol/L} \cdot \text{min}}{(0.0200\text{ mol/L})(0.0155\text{ mol/L})} = 0.371$ L/mol·min

(d) rate = (0.371 L/mol·min)(0.105 mol/L)(0.0875 mol/L) = 0.00341 mol/L· min

27. (a) $0.0168/0.00671 = (0.250/0.100)^m$; $2.50 = 2.50^m$; $m = 1$

$0.00671/0.00474 = (0.200/0.100)^n$; $1.42 = 2.00^n$; $n = 1/2$

1st order in H_2; $\frac{1}{2}$ order in Br_2

(b) rate = $k \times [H_2] \times [Br_2]^{\frac{1}{2}}$

(c) $k = \dfrac{4.74 \times 10^{-3}\text{ mol/L} \cdot \text{s}}{(0.100\text{ mol/L})(0.100\text{ mol/L})^{\frac{1}{2}}} = 0.150\ \dfrac{\text{L}^{\frac{1}{2}}}{\text{mol}^{\frac{1}{2}} \cdot \text{s}}$

(d) rate $= 0.150\ \dfrac{\text{L}^{\frac{1}{2}}}{\text{mol}^{\frac{1}{2}} \cdot \text{s}} \times 0.455\ \dfrac{\text{mol}}{\text{L}} \times (0.215)^{\frac{1}{2}}\ \dfrac{\text{mol}^{\frac{1}{2}}}{\text{L}^{\frac{1}{2}}} = 0.0316$ mol/L·s

29. (a) rate = $k \times [I^-]^m \times [BrO_3^-]^n \times [H^+]^p$

$1.78 \times 10^{-4}/0.889 \times 10^{-4} = (0.0040/0.0020)^m$; $2.0 = 2.0^m$; $m = 1$

$1.78 \times 10^{-4}/0.889 \times 10^{-4} = (0.0160/0.0080)^n$; $2.0 = 2.0^n$; $n = 1$

$3.56 \times 10^{-4}/0.889 \times 10^{-4} = (0.040/0.020)^p$; $4.0 = 2.0^p$; $p = 2$

1st order in I^- and BrO_3^-; 2nd order in H^+

(b) rate = $k \times [BrO_3^-] \times [I^-] \times [H^+]^2$

(c) $k = \dfrac{0.889 \times 10^{-4}\ \text{mol/L} \cdot \text{s}}{(0.00200\ \text{mol/L})(0.0080\ \text{mol/L})(0.020\ \text{mol/L})^2} = 1.4 \times 10^4\ \text{L}^3/\text{mol}^3 \cdot \text{s}$

(d) $5.00 \times 10^{-4}\ \dfrac{\text{mol}}{\text{L} \cdot \text{s}} = 1.4 \times 10^4\ \dfrac{\text{L}^3}{\text{mol}^3 \cdot \text{s}} \times 0.0075\ \dfrac{\text{mol}}{\text{L}} \times 0.0150\ \dfrac{\text{mol}}{\text{L}} \times [H^+]^2$

$[H^+]$ = 0.018 mol/L

31. (a) rate = $k \times [I^-]^m \times [H_2O_2]^n$

$0.0052/0.0022 = (0.035/0.015)^m$; $2.4 = 2.3^m$; $m = 1$

$0.0087/0.0052 = (0.050/0.030)^n$; $1.7 = 1.7^n$; $n = 1$

rate = $k \times [H_2O_2] \times [I^-]$

(b) $k = \dfrac{0.0022\ M/\text{min}}{0.015\ M \times 0.030\ M} = 4.9\ \dfrac{1}{M \cdot \text{min}}$

(c) mol KI = mol I^- = 0.0250 L $\times$ 0.100 mol/L = 0.00250 ; $[I^-] = \dfrac{0.00250\ \text{mol}}{(0.0250 + 0.0250)\ \text{L}} = 0.0500$ mol/L

mass H_2O_2 = 0.100 $\times$ 25.0 = 2.50 g; mol $H_2O_2 = \dfrac{2.50\ \text{g}}{34.02\ \text{g/mol}} = 0.0739$

$[H_2O_2]$ = 0.0739 mol/0.050 L = 1.47 M

rate = (4.9 L/mol·min)(0.0500 mol/L)(1.47 mol/L) = 0.36 mol/L·min

33.

time	[ ]	ln [ ]	1/[ ]
0	0.368	– 1.000	2.72
20	0.333	– 1.100	3.00
60	0.287	– 1.248	3.48
120	0.235	– 1.448	4.26
160	0.208	– 1.570	4.81

The plot of 1/[sucrose] vs t is a straight line. The reaction for the decomposition of sucrose is 2nd order.

35. (a) The plot of $\ln[(CH_3)_2N_2]$ vs t is a straight line.

(b) $k = 0.20$

(c) $\ln \dfrac{0.497}{0.100} = 0.20\,t$; $t = 8.0$ h

It takes 8.0 h to reduce the concentration from 0.497 M to 0.100 M and an additional 4.0 h to reduce the original concentration to 0.497 M. Total time is 12.0 h.

(d) rate = 0.20(0.415 M) = 0.083 mol/L·h

37. (a) $\ln \frac{0.0200\ M}{[\text{hormone}]} = \frac{3.42 \times 10^{-4}}{\text{day}}(60\ \text{day})$; [hormone] = 0.0196 M

(b) $\ln \frac{0.0200\ M}{0.00350\ M} = \frac{3.42 \times 10^{-4}}{\text{day}} \times t$; $t = 5.09 \times 10^3$ days (about 14 yr)

(c) $t_{\frac{1}{2}} = \frac{0.693}{3.42 \times 10^{-4}}$ day = 2.03×10^3 days (about 5.5 yr)

39. (a) $\ln \frac{150.0\ \text{mg}}{43.2\ \text{mg}} = k \times 0.750\ \text{h}$; $k = 1.65/\text{h}$

(b) $t_{\frac{1}{2}} = \frac{0.693}{1.65}$ h = 0.420 h

(c) $\ln \frac{1}{1 - 0.95} = \frac{1.65}{\text{h}} \times t$; $t = 1.8$ h

41. (a) $t_{\frac{1}{2}} = \frac{0.693}{1.1}$ min = (0.63 min)(60 s/min) = 38 s

(b) $\ln \frac{100\%}{\%\ PH_3\ \text{left}} = \frac{1.1}{\text{min}} \times 1.25$ min; % PH_3 left = 24%; PH_3 decomposed = (100 – 24)% = 76%

43. $2\,N_2O_5(g) \rightarrow 2\,NO_2(g) + O_2(g)$

At 0 time: mol N_2O_5 = $\frac{(756/760)\ \text{atm} \times 2.50\ \text{L}}{(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(298\ \text{K})} = 0.102$

after 135 min: $\ln \frac{0.102}{\text{mol } N_2O_5} = (0.247/\text{h})(135/60)\text{h}$; mol N_2O_5 = 0.0585

mol N_2O_5 decomposed = (0.102 − 0.0585) mol = 0.0435

mol O_2 formed = (0.0435 mol N_2O_5)(1 mol O_2/2 mol N_2O_5) = 0.022

45. $\ln \frac{5.00\ \text{mg}}{\text{mass Cu after 8 h}} = (0.0545/\text{h})(8.00\ \text{h})$; mass Cu = 3.23 mg

47. (a) $t_{\frac{1}{2}} = \frac{0.693}{6.3 \times 10^{-3}}$ min = 1.1×10^2 min

(b) $\ln \frac{100\%}{1\%} = \frac{6.3 \times 10^{-3}}{\text{min}} \times t$; $t = 7.3 \times 10^2$ min

49. (a) $k = \frac{A_o}{2(t_{\frac{1}{2}})} = \frac{0.188\ M}{(2)(315\ \text{min})} = 2.98 \times 10^{-4}\ M/\text{min}$

(b) $t = \frac{[A_o] - [A]}{k} = \frac{(0.219 - 0)\ M}{2.98 \times 10^{-4}\ M/\text{min}} = 735$ min

(c) rate = $k[A]^0 = 2.98 \times 10^{-4}\ M$/min

(d) Rate does not change.

51. (a) rate = $\dfrac{(1.00 - 0.200)\text{ atm}}{16\text{ s}}$ = 0.050 atm/s; k = rate = 0.050 atm/s

(b) $t = \dfrac{(P_o - P_t)}{k} = \dfrac{(0.150 - 0.0432)\text{ atm}}{0.050\text{ atm/s}}$ = 2.1 s

(c) $t_{\frac{1}{2}} = P_o/2k$ = 0.500 atm/2(0.050 atm/s) = 5.0 s

53. (a) $k = \dfrac{1}{[A_o]k} = \dfrac{1}{(1.51\text{ min})(0.250\text{ mol/L})}$ = 2.65 L/mol·min

(b) $t = \dfrac{1/[A] - 1/[A_o]}{k} = \dfrac{(1/0.0915) - (1/0.187)\text{ L/mol}}{2.65\text{ L/mol}\cdot\text{min}}$ = 2.11 min

(c) rate = (2.65 L/mol · min)(0.335 mol/L)^2 = 0.297 mol/L · min

55. Decomposing 90% means [A] = 0.10[A_o]

$$t = \frac{1/[A] - 1/[A_o]}{k} = \frac{[(1/(0.10)(0.02) - (1/0.02)]\text{ L/mol}}{48\text{ L/mol}\cdot\text{min}} = 9.4\text{ min}$$

57. k at 293 K; 2k at 303 K

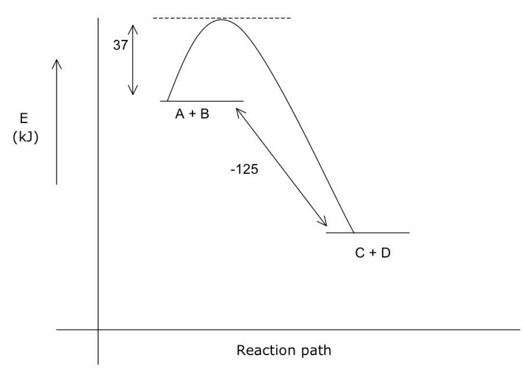
$$\ln\frac{2k}{k} = \frac{E_a}{0.00831\text{ kJ/mol}\cdot\text{K}}\left(\frac{1}{293\text{ K}} - \frac{1}{303\text{ K}}\right); \quad E_a = 51.1\text{ kJ/mol}$$

59.

ln k	-4.556	-2.293	-0.511	1.072
$1/T$	1.43×10^{-3}	1.33×10^{-3}	1.25×10^{-3}	1.18×10^{-3}

slope $\approx \dfrac{-5.63}{2.5\times10^{-4}} = \dfrac{-E_a}{R}$; $E_a = (8.31\times10^{-3}\text{ kJ})(2.25\times10^4) \approx 1.9\times10^2$ kJ

61.



63. (a) $t_{\frac{1}{2}} = \dfrac{0.693}{4.90 \times 10^{-4}}$ min = 1.41×10^3 min

(b) $\ln \dfrac{k \text{ at } 40°\text{C}}{4.90 \times 10^{-4}\ \text{min}^{-1}} = \dfrac{420\ \text{kJ/mol}}{0.00831\ \text{kJ/mol}\cdot\text{K}}\left(\dfrac{1}{310\ \text{K}} - \dfrac{1}{313\ \text{K}}\right);$ k at 40°C = 0.00234 min^{-1}

$t_{\frac{1}{2}} = \dfrac{0.693}{2.34 \times 10^{-3}}$ min = 3.0×10^2 min

(c) $\dfrac{1.41 \times 10^3}{3.0 \times 10^2}$ min = 5.0 times as long, so rate is 5.0 times faster over a 3° rise ≈ 1.7 times/°C rise

65. Let k_1 be the constant at 21°C and k_2 the constant at 5°C.

$\ln \dfrac{k_1}{k_2} = \dfrac{75\ \text{kJ/mol}}{0.00831\ \text{kJ/mol}\cdot\text{K}}\left(\dfrac{1}{278\ \text{K}} - \dfrac{1}{294\ \text{K}}\right);$ $k_1/k_2 = 5.9$

Let t_1 be the souring time at 21°C and t_2 the souring time at 5°C.

$\dfrac{k_1}{k_2} = \dfrac{t_2}{t_1};$ $t_2 = 5.9(8\ \text{h}) = 47\ \text{h} \approx 2$ days

67. (a) $\ln \dfrac{22.8}{0.066} = \dfrac{E_a}{0.00831\ \text{kJ/mol}\cdot\text{K}}\left(\dfrac{1}{838\ \text{K}} - \dfrac{1}{1001\ \text{K}}\right);$ $E_a = 2.50 \times 10^2$ kJ/mol

(b) $\ln \dfrac{22.8}{k} = \dfrac{2.50 \times 10^2\ \text{kJ/mol}}{0.00831\ \text{kJ/mol}\cdot\text{K}}\left(\dfrac{1}{758\ \text{K}} - \dfrac{1}{1001\ \text{K}}\right);$ $k = 1.49 \times 10^{-3}$ L/mol · min

(c) $\ln \dfrac{22.8}{11.6} = \dfrac{2.50 \times 10^2\ \text{kJ/mol}}{0.00831\ \text{kJ/mol}\cdot\text{K}}\left(\dfrac{1}{T} - \dfrac{1}{1001\ \text{K}}\right);$ T = 979 K = 706°C

69. At 477°C: $k = 0.693/5.00 = 0.128$ min^{-1}

$\ln \dfrac{k_2}{0.128} = \dfrac{262\ \text{kJ/mol}}{0.00831\ \text{kJ/mol}\cdot\text{K}}\left(\dfrac{1}{750\ \text{K}} - \dfrac{1}{800\ \text{K}}\right);$ $k_2 = 1.77$ min^{-1}

$t_{\frac{1}{2}} = 0.693/1.77$ min^{-1} = 0.391 min = 23 s

71. E_a for the uncatalyzed reverse reaction = E_a for the forward reaction $-\ \Delta H$ = 135 kJ – 45 kJ = 90 kJ

73. $\ln k_{\text{uncat}} = \ln A - \dfrac{1}{RT}(E_{\text{auncat}});$ $\ln k_{\text{cat}} = \ln A - \dfrac{1}{RT}(E_{\text{acat}})$

$\ln k_{\text{cat}} - \ln k_{\text{uncat}} = -\dfrac{1}{RT}(E_{\text{acat}}) - \left[-\dfrac{1}{RT}(E_{\text{auncat}})\right]$

$\ln \dfrac{k_{\text{cat}}}{k_{\text{uncat}}} = \dfrac{1}{RT(E_{\text{auncat}} - E_{\text{acat}})} = \dfrac{1}{(0.00831\ \text{kJ/mol}\cdot\text{K})(298\ \text{K})}(215 - 206) = 38$

The rate constant increases by a factor of 38.

75. (a) rate = $k\,[NO_3][CO]$ (b) rate = $k\,[I_2]$ (c) rate = $k\,[O_2][NO]$

77. rate = $k\,[H_2][I]^2$; $k_1\,[I_2] = k_2[I]^2$; $[I]^2 = \dfrac{k_1\,[I_2]}{k_2}$; rate = $\dfrac{k\,k_1}{k_2}\,[H_2][I_2]$

79. (a) rate = $k\,[CO][NO_2]$; no

(b) rate = $k\,[N_2O_4][CO]^2 = \dfrac{k\,k_1}{k_2}\,[NO]^2[CO]^2$; no

(c) rate = $k\,[NO_2]^2$; yes

(d) rate = $k\,[NO_2]^2$; yes

81. (a) Since the plot of $1/[A_2B_2]$ vs time is linear, the reaction is second order. rate = $k\,[A_2B_2]^2$

(b) slope = $k = 0.137/M \cdot \text{min}$

(c) $t_{\frac{1}{2}} = \dfrac{1}{(0.137\ M^{-1}\text{min}^{-1})(0.631\ M)} = 11.6$ min

(d) rate = $\dfrac{0.137}{M \cdot \text{min}}\,(0.219\ M)^2 = 6.57 \times 10^{-3}\ M/\text{min}$

(e) $\dfrac{1}{[A_2B_2]} - \dfrac{1}{0.822} = 0.137(8.6)$; $[A_2B_2] = 0.418\ M$

83. (a) $k = \dfrac{0.693}{7.5 \times 10^2\ \text{min}} = 9.24 \times 10^{-4}\ \text{min}^{-1}$

$\ln \dfrac{122\ \text{g}}{45\ \text{g}} = 9.24 \times 10^{-4}\ \text{min}^{-1}\,(t)$; $t = 18$ h

(b) $\ln \dfrac{122\ \text{g}}{\text{mass } SO_2Cl_2 \text{ left}} = 9.24 \times 10^{-4}\ \text{min}^{-1}\,(29\ \text{h})\,(60\ \text{min/h})$; mass SO_2Cl_2 left = 24.4 g

moles Cl_2 formed = moles SO_2Cl_2 decomposed = $\dfrac{(122 - 24.4)\ \text{g}}{135\ \text{g/mol}} = 0.723$

$V = \dfrac{(0.723\ \text{mol})(0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K})(300\ \text{K})}{1.00\ \text{atm}} = 17.8\ \text{L}$

85. $\ln \dfrac{k_2}{k_1} = \dfrac{85\ \text{kJ/mol}}{0.00831\ \text{kJ/mol} \cdot \text{K}} \left(\dfrac{1}{298\ \text{K}} - \dfrac{1}{303\ \text{K}}\right)$; $\dfrac{k_2}{k_1} = 1.8$

If $k_1 = 1$, then $k_2 = 1.8$; an increase of 0.8 or 80%

87. $-\Delta[A] = k\Delta t$; $\Delta[A] = [A] - [A]_o$ and $\Delta t = t - 0$

$-([A] - [A]_o) = k(t - 0)$; $[A] = [A]_o - kt$

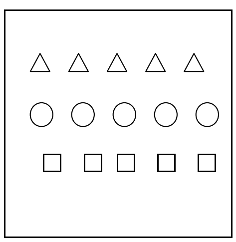
89. (a) increases by a factor of 1.4 (b) cuts rate in half (c) rate is 7/10 of original

(d) increases by a factor of 2.8 (e) has greatest effect

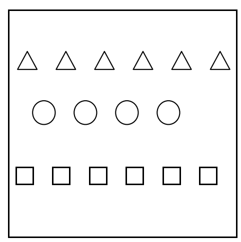
91. second order; half life is inversely proportional to the original concentration

93. (a) F (b) T (c) F (d) T (e) F (f) F

95. after 3 minutes:



after 4 minutes:



97. (a) (1)

(b) Rate and k increase; E_a remains the same.

99. (a) ΔH° = 52.96 kJ − 62.44 kJ = −9.48 kJ; E_a for the reverse reaction = 165 kJ + 9 kJ = 174 kJ

(b) $\dfrac{k_{reverse}}{k} = \dfrac{e^{-E_{a_{reverse}}/RT}}{e^{-E_a/RT}} = e^{(E_a - E_{a_{reverse}})/RT} = e^{-9/(0.00831)(973)} = 0.33$

$138\ \dfrac{L}{mol \cdot s} \times 0.33 = 46\ \dfrac{L}{mol \cdot s}$

(c) rate = $46\ \dfrac{L}{mol \cdot s} \times (0.200\ mol/L)^2 = 1.8\ mol/L \cdot s$

100. At 100°C, rate constant = k_2; at 87°C, rate constant = k_1

$\ln \dfrac{k_2}{k_1} = \dfrac{69\ kJ/mol}{0.00831\ kJ/mol \cdot K}\left(\dfrac{1}{373\ K} - \dfrac{1}{360\ K}\right)$; $\dfrac{k_2}{k_1} = 2.23$; $k_2 = 2.23\ k_1$

$\ln \dfrac{[A_o]}{[A]} = k_2(5.4)$; $\ln \dfrac{[A_o]}{[A]} = k_1(t)$; $k_2(5.4) = k_1(t)$; $2.23\ (k_1)(5.4) = k_1(t)$; $t = 12$ min

101. $-\frac{1}{a}\frac{d[\text{A}]}{dt} = k[\text{A}]; \quad -\frac{d[\text{A}]}{[\text{A}]} = ak\,dt; \quad \ln\frac{[\text{A}_\text{o}]}{[\text{A}]} = akt$

102. Compare 1st and 4th: second order in A

Compare 2nd and 4th: first order in C

Compare 1st and 3rd: change in [C] should double rate, so must be first order in B

rate = $k[\text{A}]^2[\text{B}][\text{C}]$

103. (a) $-\frac{d[\text{A}]}{dt} = k[\text{A}]^2; \quad -\frac{d[\text{A}]}{[\text{A}]^2} = k\,dt; \quad \frac{1}{[\text{A}]} - \frac{1}{[\text{A}_\text{o}]} = kt$

(b) $-\frac{d[\text{A}]}{[\text{A}]^3} = k\,dt; \quad \frac{1}{2[\text{A}]^2} - \frac{1}{2[\text{A}_\text{o}]^2} = kt$

104. $a = 0.30 \times \frac{8\text{ h}}{48\text{ h}} = 0.050$; saturation value = $\frac{0.100\text{ g}}{1 - 10^{-0.050}} = 0.91$ g

$0.500 = X/0.11$; $X = 0.055$ g